

PATENT SPECIFICATION

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(19)



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(54) NICKEL BASE ALLOY CONTAINING HAFNIUM

(71) We, AVCO CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Suite 1800, 1014 Vine Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to nickel base alloys exhibiting high strength, stability, ductility and resistance to corrosion, sulfidation and oxidation at elevated temperatures and which are useful for blades, vanes and integrally cast turbine wheels.

The nickel base alloys of this invention contain relatively small, but nonetheless significant, amounts of tungsten and molybdenum for solid solution strengthening; chromium for oxidation and sulfidation resistance; tantalum for solid solution and carbide strengthening; aluminum and titanium to enhance the strength by precipitation of a fine dispersed phase, gamma prime (Ni₃(Al, Ti)), and hafnium for intermediate strength, ductility and improved oxidation resistance.

Compositions of the following analyses are contemplated as within the scope of the present invention the compositions being expressed in weight percent, the balance being Ni except for incidental impurities:

| | | | | | |
|----|---|-----------|---------|---|-------------|
| C | — | 0.30 max. | Hf | — | 0.1—3 |
| Cr | — | 11—15 | Ti | — | 3.5—4.5 |
| Co | — | 8—12 | Al | — | 3—4 |
| Mo | — | 1—2.5 | Ti + Al | — | 7—8 |
| W | — | 3—10 | B | — | 0.005—0.025 |
| Ta | — | 3.5—10 | Zr | — | 0.05—0.4 |

balance Ni

A more preferred range of composition is as follows:

| | | | | | |
|----|---|----------|------------|---|-------------|
| C | — | .25 max. | Hf | — | 0.4—3 |
| Cr | — | 11—13.5 | Ti | — | 3.5—4.5 |
| Co | — | 8—11 | Al | — | 3—4 |
| Mo | — | 1—2.5 | Ti + Al | — | 7—8 |
| W | — | 3—5 | B | — | 0.005—0.025 |
| Ta | — | 3.5—8 | Zr | — | 0.05—0.4 |
| | | | Balance Ni | | |

A still more preferred range of compositions is as follows (in weight percent):

| | | | | | | |
|----|------------|---|------------------------|---------|---|-----------|
| 5 | C | — | 0.10—0.22 | Hf | — | 0.75—1.25 |
| | Cr | — | 12.2—13.5 | Ti | — | 3.9—4.2 |
| | Co | — | 8.5—9.5 | Al | — | 3.2—3.6 |
| | Mo | — | 1.85—2.05 | Ti + Al | — | 7.25—7.70 |
| | W | — | 3.65—8 | B | — | 0.01—0.02 |
| 10 | | | (preferably 3.65—4.05) | | | |
| | Ta | — | 3.65—8 | Zr | — | .08—.25 |
| | | | (preferably 3.65—4.05) | | | |
| | balance Ni | | | | | |

Exemplary alloys in accordance with the teachings of this invention had the compositions shown in Table I which follows:

TABLE I

| Heat No. | C | Cr | Ce | Mo | W | Ta | Hf | Ti | Al | Ti+Al | B | Zr | Ni |
|-------------|-----|-------|------|------|------|------|------|------|------|-------|------|-----|-----|
| I | .15 | 12.50 | 9.35 | 1.94 | 3.99 | 3.86 | 1.10 | 3.96 | 3.57 | 7.53 | .015 | .17 | Bal |
| II | .15 | 12.50 | 9.35 | 1.94 | 3.99 | 3.86 | 2.28 | 3.96 | 3.57 | 7.53 | .015 | .21 | Bal |
| III | .23 | 12.80 | 8.68 | 1.97 | 4.00 | 3.77 | 0.49 | 4.32 | 3.28 | 7.60 | .016 | .13 | Bal |
| IV | .23 | 12.38 | 8.68 | 1.97 | 4.00 | 3.77 | 1.07 | 4.32 | 3.28 | 7.60 | .016 | .16 | Bal |
| V | .23 | 12.38 | 8.68 | 1.97 | 4.00 | 3.77 | 1.55 | 4.32 | 3.28 | 7.60 | .016 | .14 | Bal |
| VI | .23 | 12.38 | 8.68 | 1.97 | 4.00 | 3.77 | 1.80 | 4.32 | 3.28 | 7.60 | .016 | .20 | Bal |
| VII | .23 | 12.38 | 8.68 | 1.97 | 4.00 | 3.77 | 0.44 | 4.32 | 3.28 | 7.60 | .016 | .14 | Bal |
| VIII | .20 | 12.31 | 9.18 | 1.94 | 3.72 | 4.05 | 1.06 | 4.08 | 3.38 | 7.46 | .014 | .15 | Bal |
| IX | .20 | 12.31 | 9.18 | 1.94 | 3.72 | 4.05 | 2.26 | 4.08 | 3.38 | 7.46 | .014 | .22 | Bal |
| X | .20 | 12.31 | 9.18 | 1.94 | 3.72 | 4.05 | 2.16 | 4.08 | 3.38 | 7.46 | .014 | .21 | Bal |
| XI | .20 | 12.31 | 9.18 | 1.94 | 3.72 | 4.05 | 1.16 | 4.08 | 3.38 | 7.46 | .014 | .16 | Bal |
| XII | .19 | 12.66 | 9.42 | 1.92 | 3.75 | 3.86 | 2.40 | 4.01 | 3.27 | 7.28 | .015 | .22 | Bal |
| XIII | .15 | 12.50 | 8.88 | 2.04 | 3.95 | 5.0 | 1.13 | 3.96 | 3.22 | 7.18 | .013 | .10 | Bal |
| XIV | .15 | 12.50 | 8.88 | 2.04 | 3.95 | 6.0 | 1.13 | 3.96 | 3.22 | 7.18 | .013 | .10 | Bal |
| XV | .20 | 13.35 | 8.88 | 1.91 | 3.87 | 8.0 | 1.20 | 4.18 | 3.21 | 7.39 | .012 | .11 | Bal |

TABLE I (cont'd)

| Heat No. | C | Cr | Co | Mo | W | Ta | Hf | Ti | Al | Ti+Al | B | Zr | Ni |
|----------|-----|-------|-------|------|------|------|------|------|------|-------|------|-----|-----|
| XVI | .20 | 13.35 | 10.88 | 1.91 | 3.87 | 6.0 | 1.20 | 4.18 | 3.21 | 7.39 | .012 | .11 | Bal |
| XVII | .20 | 13.35 | 10.88 | 1.91 | 3.87 | 7.0 | 1.20 | 4.18 | 3.21 | 7.39 | .012 | .11 | Bal |
| XVIII | .20 | 13.35 | 10.88 | 1.91 | 3.87 | 8.0 | 1.20 | 4.18 | 3.21 | 7.39 | .012 | .11 | Bal |
| XIX | .15 | 12.87 | 9.49 | 2.01 | 4.01 | 4.0 | 1.05 | 4.10 | 3.23 | 7.33 | .013 | .11 | Bal |
| XX | .15 | 12.87 | 9.49 | 2.01 | 5.01 | 7.50 | 1.05 | 4.10 | 3.23 | 7.33 | .013 | .11 | Bal |
| XXI | .15 | 12.87 | 9.49 | 2.01 | 7.50 | 5.0 | 1.05 | 4.10 | 3.23 | 7.33 | .013 | .11 | Bal |
| XXII | .15 | 12.87 | 9.49 | 2.01 | 10.0 | 5.0 | 1.05 | 4.10 | 3.23 | 7.33 | .013 | .11 | Bal |
| XXIII | .16 | 12.60 | 9.40 | 2.0 | 3.97 | 3.85 | 0.50 | 4.0 | 3.55 | 7.55 | .020 | .10 | Bal |
| XXIV | .21 | 12.80 | 9.40 | 2.19 | 4.0 | 4.08 | 1.95 | 4.05 | 3.25 | 7.30 | .014 | .10 | Bal |
| XXV | .21 | 12.80 | 9.40 | 2.19 | 4.0 | 4.08 | 1.95 | 4.05 | 3.25 | 7.30 | .014 | .15 | Bal |
| XXVI | .21 | 12.80 | 9.40 | 2.19 | 4.0 | 4.08 | 1.95 | 4.05 | 3.25 | 7.30 | .014 | .20 | Bal |
| XXVII | .09 | 12.30 | 9.10 | 1.87 | 7.40 | 4.94 | 1.25 | 4.18 | 3.35 | 7.53 | .012 | .12 | Bal |
| XXVIII | .09 | 12.30 | 9.10 | 1.87 | 4.90 | 4.94 | 1.25 | 4.18 | 3.35 | 7.53 | .012 | .12 | Bal |
| XXIX | .27 | 12.40 | 9.00 | 1.87 | 7.40 | 4.90 | 1.15 | 4.06 | 3.20 | 7.26 | .013 | .11 | Bal |

5 After vacuum melting, the alloys noted
above were vacuum cast into test bars and sub-
jected to stress rupture testing according to
ASTM Standard E139. The test bars were
10 heat treated before testing as follows: heated to
2050°F, held at that temperature for two (2)
hours then air cooled, then reheated to 1550°F
and held at 1550°F for four (4) hours, then
air cooled, then reheated to 1400°F and held
15 at that temperature for 16 hours then air
cooled.

After the heat treatment described above,
stress rupture tests were conducted on cast
test bars representative of each of the heats
15 in the heat treated condition at 1400°F/

90Ksi, 1400°F/100Ksi, 1700°F/39Ksi and
1800°F/29Ksi. The results are given in Table
II, it being noted that thickwall data refers to
0.250" diameter solid test bar results. Thin-
wall data refers to tubular test bar results in 20
which wall thickness is 0.040". Thickwall or
solid test for data reflects mechanised property
capability of heavy sections such as might be
represented by turbine blade roots. Thin wall 25
or tubular test bar properties reflect the
mechanical property capabilities of thin walled
sections such as might be represented by cored
or hollow turbine blade airfoils. Thinwall data
are for tests at 1700°F/35Ksi.

TABLE II
STRESS RUPTURE TEST RESULTS

| Heat No. | 1400°F/90Ksi Life (Hrs.) | 1400°F/90Ksi El (%) | 1400°F/95Ksi Life (Hrs.) | 1400°F/95Ksi El (%) | THICKWALL 1400°F/100Ksi Life (Hrs.) | THICKWALL 1400°F/100Ksi El (%) | 1700°F/39Ksi Life (Hrs.) | 1700°F/39Ksi El (%) | 1800°F/29Ksi Life (Hrs.) | 1800°F/29Ksi El (%) | THINWALL 1700°F/35Ksi Life (Hrs.) | THINWALL 1700°F/35Ksi El (%) |
|----------|-----------------------------|------------------------|-----------------------------|------------------------|---|--------------------------------------|-----------------------------|------------------------|-----------------------------|------------------------|---|------------------------------------|
| I | 462 | 4 | 163 | 3 | | | 72 | 5 | | | | |
| | 483 | 5 | | | | | 99 | 5 | | | | |
| II | | | 382 | 7 | | | 79 | 9 | | | | |
| III | | | 225 | 5 | | | 99 | 10 | | | | |
| | | | 87 | 10 | | | 106 | 10 | | | | |
| IV | | | 211 | 5 | | | 106 | 10 | | | | |
| | | | 180 | 5 | | | | | | | | |
| V | | | 73 | 3 | | | | | | | | |
| | | | 119 | 5 | | | 48 | 8 | | | | |
| VI | | | 208 | 4 | | | 77 | 9 | | | | |
| VII | 277 | 4 | | | | | 65 | 7 | | | | |
| | 419 | 5 | | | | | 121 | 3 | | | | |
| VIII | 286 | 5.5 | | | | | 50 | 8 | | | | |
| | 408 | 6 | | | | | 37 | 6 | | | | |
| IX | 530 | 3 | | | | | 45 | 10 | | | | |
| | | | | | | | 38 | 6 | | | | |
| | | | | | | | 36 | 7 | | | | |

TABLE II (cont'd)
STRESS RUPTURE TEST RESULTS

| Heat No. | 1400°F/90Ksi | | 1400°F/95Ksi | | THICKWALL 1400°F/100Ksi | | 1700°F/39Ksi | | 1800°F/29Ksi | | THINWALL 1700°F/35Ksi | |
|-------------|----------------|-----------|----------------|-----------|----------------------------|-----------|----------------|-----------|----------------|-----------|--------------------------|-----------|
| | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) |
| XVII | | | | | 130 | 8 | 93 | 7 | 38 | 10 | | |
| | | | | | | | | | 45 | 9 | | |
| XVIII | | | | | | | | | 35 | 9 | | |
| | | | | | | | | | 37 | 8 | | |
| XIX | | | | | 130 | 9 | 72 | 9 | | | 53 | 6 |
| | | | | | 103 | 8 | | | | | 58 | 6 |
| XX | | | | | 149 | 4 | | | 50 | 6 | 64.4 | 6.0 |
| | | | | | 174 | 4 | | | 28 | 9 | 70.6 | 5.0 |
| | | | | | | | | | | | 178.0 | 5.0 |
| XXI | | | | | 142 | 4 | | | 43 | 10 | 129 | 5 |
| | | | | | 224 | 5 | | | 79 | 5 | 189 | 5 |
| | | | | | | | | | 81 | 7 | 254 | 5 |
| XXII | | | | | 224 | 5 | | | 45 | 5 | 101 | N/A |
| | | | | | | | | | 51 | 8 | 137 | 6 |
| XXIII | 113 | 4 | | | | | 39 | 4 | | | | |
| | 116 | 3 | | | | | 67 | 4 | | | | |

N.A Not Available.

TABLE II (cont'd)
STRESS RUPTURE TEST RESULTS

| Heat No. | 1400°F/90Ksi Life (Hrs.) | 1400°F/95Ksi Life (Hrs.) | THICKWALL 1400°F/100Ksi Life (Hrs.) | THICKWALL 1400°F/100Ksi El (%) | 1700°F/39Ksi Life (Hrs.) | 1700°F/39Ksi El (%) | 1800°F/29Ksi Life (Hrs.) | 1800°F/29Ksi El (%) | THINWALL 1700°F/35Ksi Life (Hrs.) | THINWALL 1700°F/35Ksi El (%) |
|----------|-----------------------------|-----------------------------|---|--------------------------------------|-----------------------------|------------------------|-----------------------------|------------------------|---|------------------------------------|
| XXIV | | | 144 | 9 | 109 | 10 | | | | |
| | | | 167 | 6 | 88 | 10 | | | | |
| | | | | | 99 | 10 | | | | |
| XXV | | | 181 | 15 | 65 | N/A | | | | |
| | | | | | 71 | 8 | | | | |
| XXVI | | | 172 | 6 | 79 | 10 | | | | |
| | | | 168 | 8 | 83 | 8 | | | | |
| | | | | | 80 | 9 | | | | |
| XXVII | | | 163 | 5 | | | 59 | 8 | 60 | 3 |
| | | | 157 | 7 | | | 58 | 5 | 68 | 4 |
| XXVIII | | | 130 | 4 | 119 | 8 | 60 | 10 | 111 | 5 |
| | | | 212 | 6 | 75 | 9 | 61 | 9 | 125 | 5 |
| | | | | | | | | | 125 | 9 |
| XXIX | | | 110 | 4 | | | 81 | 5 | 122 | 4 |
| | | | 133 | 5 | | | 61 | 8 | 184 | 4 |
| | | | | | | | | | 212 | 5 |

N.A. Not available.

TABLE II (cont'd)
STRESS RUPTURE TEST RESULTS

| Heat No. | 1400°F/90Ksi | | 1400°F/95Ksi | | THICKWALL 1400°F/100Ksi | | 1700°F/99Ksi | | 1800°F/29Ksi | | THINWALL 1700°F/35Ksi | |
|---------------|----------------|-----------|----------------|-----------|----------------------------|-----------|----------------|-----------|----------------|-----------|--------------------------|-----------|
| | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) | Life (Hrs.) | El (%) |
| INCO 713 | 16 | 6 | 5 | 4 | | | 20 | 12 | | | | |
| MAR-M- 421 | 50 | 3 | 20 | 3 | | | 15 | 15 | | | | |
| IN792 | 255 | 7.5 | | | 75 | 7 | 75 | 9 | | | | |

Corresponding values for three presently known commercial alloys are appended to Table II for comparison.

5 INCO 713C is reported to be an alloy with a nominal composition of

C Cr Mo W Cb Ti Al
0.14 13.0 4.5 0.20 2.0 0.75 5.75

Zr B Ni
0.05 0.012 Balance

10

MAR-M-421 is reported to be an alloy with

a nominal composition of

C Cr Co Mo W Cb Ti Al
0.15 15.8 9.5 2.0 3.8 2.0 1.8 4.3

Zr B Ni
0.05 0.015 Balance

INCO IN792 is reported to be the alloy described in United States Patent 3,619,182.

Table III presents the room temperature tensile properties of the alloy of this invention, heat treated as before, after casting into test bars.

20

TABLE III
ROOM TEMPERATURE TENSILE TEST RESULTS

| Heat No. | Uts. (Ksi) | 0.2% Y.S. (Ksi) | (%) | R.A. (%) |
|-----------|------------|-----------------|-----|----------|
| VIII | 181.4 | 169.2 | 3.5 | 3.2 |
| | 172.5 | 163.9 | 3.5 | 3.2 |
| INCO-713C | 123 | 106 | 7.9 | 11.6 |
| MAR-M-421 | 150 | 130 | 3.5 | 5 |

Comparable values for the same commercial alloys are appended to the table for comparison.

- 5 In the Tables IV and V respectively, data is presented on cyclic oxidation test results conducted at 1750°F and hot corrosion test conducted at 1650°F.

10 TABLE IV
COMPARATIVE CYCLIC OXIDATION
TEST RESULTS

| Material | Weight Change (Mg/Cm ²) After 240 Hours at 1750°F |
|-----------|--|
| Heat VIII | 1.15 |
| Heat IX | 0.95 |
| INCO 713C | -4.40 |
| MAR-M-421 | -2.20 |

20 TABLE V
COMPARATIVE HOT CORROSION
TEST RESULTS

| Material | Depth of Attack (Mils) After 150 Hours at 1650°F with 6 ppm Salt |
|-----------|--|
| Heat VIII | 4.2 |
| INCO 713C | 26.0 |
| MAR-M-421 | 15.0 |

- 30 It is not intended that the invention sought to be patented be limited by the foregoing description, but merely by the scope of the appended claims.

WHAT WE CLAIM IS:—

- 35 1. A nickel base alloy exhibiting high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:

| | | |
|-------|---|-------------|
| C | — | .30 max. |
| Cr | — | 11—15 |
| Co | — | 8—12 |
| Mo | — | 1—2.5 |
| W | — | 3—10 |
| Ta | — | 3.5—10 |
| Hf | — | 0.1—3 |
| Ti | — | 3.5—4.5 |
| Al | — | 3—4 |
| Ti+Al | — | 7—8 |
| B | — | 0.005—0.025 |
| Zr | — | .05—.40 |
| Ni | — | Balance |

40

45

2. A nickel base alloy exhibiting high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:

| | | |
|-------|---|-------------|
| C | — | .25 max. |
| Cr | — | 11—13.5 |
| Co | — | 8—11 |
| Mo | — | 1—2.5 |
| W | — | 3—5 |
| Ta | — | 3.5—8 |
| Hf | — | 0.4—3.0 |
| Ti | — | 3.5—4.5 |
| Al | — | 3—4 |
| Ti+Al | — | 7—8 |
| B | — | 0.005—0.025 |
| Zr | — | .05—.40 |
| Ni | — | Balance |

55

60

65

3. A nickel base alloy exhibiting high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:

70

| 12 | 1,409,628 | | | | | | 12 |
|----|--|---|-----------|---|---|-------------|----|
| | C | — | .10—.22 | Ta | — | 3.65—8 | |
| | Cr | — | 12.2—13.5 | Hf | — | 0.75—1.25 | 25 |
| | Co | — | 8.50—9.50 | Ti | — | 3.9—4.2 | |
| | Mo | — | 1.85—2.05 | Al | — | 3.2—3.6 | |
| 5 | W | — | 3.65—4.05 | Ti+Al | — | 7.25—7.70 | |
| | Ta | — | 3.65—4.05 | B | — | 0.010—0.020 | |
| | Hf | — | 0.75—1.25 | Zr | — | 0.08—0.25 | 30 |
| | Ti | — | 3.90—4.20 | Ni | — | Balance | |
| | Al | — | 3.20—3.60 | | | | |
| 10 | Ti+Al | — | 7.25—7.70 | 5. A nickel base alloy according to Claim 1 which has been heat treated. | | | |
| | B | — | .010—.020 | 6. A nickel base alloy as claimed in Claims 1 to 5 substantially as hereinbefore described. | | | |
| | Zr | — | 0.08—0.25 | 7. An article formed of the alloy according to any one of the preceding claims. | | | |
| | Ni | — | Balance | 8. A vacuum cast article consisting of the alloy of any one of the preceding Claims 1 to 6. | | | |
| 15 | 4. A nickel base alloy exhibiting, high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent: | | | | | | 40 |
| | C | — | .10—.22 | For the Applicants:— | | | |
| 20 | Cr | — | 12.2—13.5 | F. J. CLEVELAND & COMPANY, | | | |
| | Co | — | 8.5—9.5 | Chartered Patent Agents, | | | |
| | Mo | — | 1.85—2.05 | Lincoln's Inn Chambers, | | | |
| | W | — | 3.65—8 | 40—43 Chancery Lane, | | | |
| | | | | London, W.C.2. | | | |

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